

Vibrational-state spectrum in amorphous materials with a molecular structure

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The vibrational-state density has been determined experimentally for a solid phase with a liquid-crystal structure. There is a change in the frequency spectrum at the transition to an ordered crystalline state.

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In this letter we are reporting experiments on glassy materials with molecular structure, which have received little previous study. Broude¹ was the first to point out that complex aromatic compounds of mono- and polyalkyl-substituted benzene are distinguished by a significant supercooling, and rapid freezing causes them to form a glassy material. Most of the compounds studied by Broude exhibited polymorphic transformations in a narrow temperature range near the melting point. A similar behavior has been observed in a study of mesogens.²⁻⁶ It has been found that the glassy material formed by freezing nematic liquid crystals is disordered in its initial phase. In this letter we are reporting the first attempt to study the effect of a disorder of this type on the vibrational-state spectrum of a solid phase by studying the spectra of incoherent inelastic neutron scattering. Since these measurements can be carried out at low temperatures, multiphonon effects are minimized, and anharmonic effects are substantially reduced.

The incoherent inelastic neutron scattering spectra (Fig. 1) were recorded at 5 K from the glassy phase and from one of the solid crystalline phases of the classic nematic crystal MBBA (*p*-methoxy benzylidene *p*-butylaniline) and at 300 K from a liquid-crystal phase. The spectra were measured by a time-of-flight method with a KDSOG inverted-geometry spectrometer at the IBR-30 reactor of the Neutron Physics Laboratory, Joint Institute for Nuclear Research. The glassy phase¹ was obtained by cooling a liquid-crystal sample at a rate of 50 deg/min. The solid crystalline phase was obtained by heating the glassy sample to 287 K and holding it there for 150 h.

Since the incoherent inelastic neutron scattering spectra of the solid phases of molecular compounds correspond to single phonons (or single quanta) at low temperatures, the structure of these spectra can be related to the structure of the harmonic vibrational-state density $G_H(\nu)$, weighted by the square displacement amplitudes of the atoms (primarily, hydrogen atoms).⁷ Figure 2 shows the functions $G_H(\nu)$ found from the experimental spectra (Fig. 1) [see Ref. 8 regarding the validity of extracting $G_H(\nu)$ from the experimental incoherent inelastic neutron scattering spectrum]. Experience with polyatomic molecular systems has shown that in the molecular-vibration region the functions $G_H(\nu)$ are very similar in shape to the vibrational-state density. In the scattering spectrum of the liquid crystal (Fig. 1A) both multiquantum

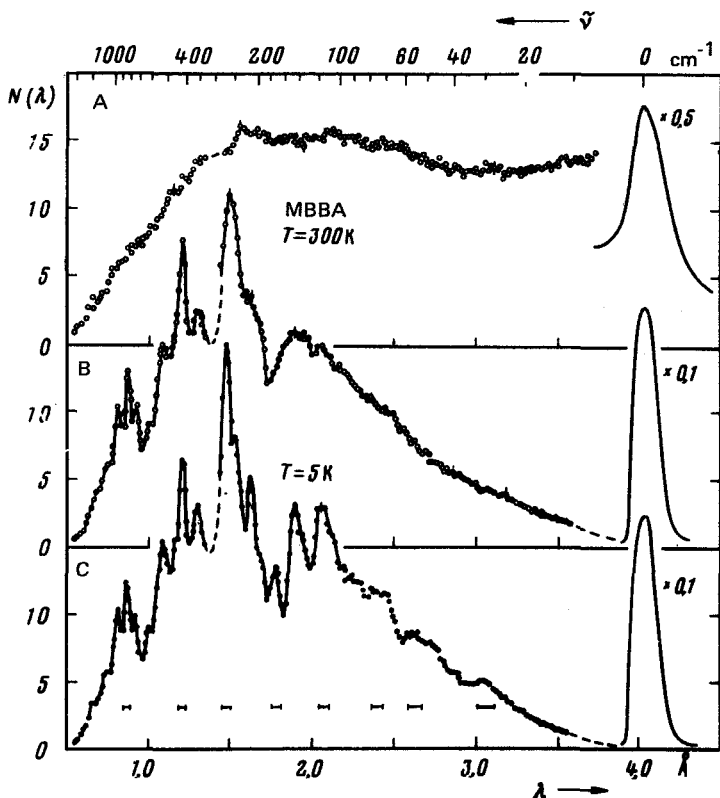


FIG. 1. Incoherent inelastic neutron scattering spectra of various phases of MBBA. A—Liquid crystal, B—glassy phase; C—crystalline solid. λ —wavelength of the neutrons incident on the sample; $N(\lambda)$ —normalized intensity of the scattered neutrons; horizontal line segments—resolution of the spectrometer. The energy transfer ν is reckoned from the position of the elastic-scattering peak; the cassette holding the sample has dimensions of $18 \times 16 \times 0.08$ cm; the average measurement time is 45 h.

scattering processes and anharmonic effects are important. The spectrum of the glassy phase (Fig. 1B) can be described as the single-quantum harmonic component of the vibrational spectrum of the liquid crystal. It then follows, in particular, that in the region of low-frequency molecular vibrations ($\nu < 200$ cm^{-1}) the vibrational-state density of a nematic liquid crystal has no structural features, as is also the case for $G_H(\nu)$ for a frozen sample (Fig. 2A).

The transition from a frozen liquid-crystal structure to a crystal is not accompanied by any radical change in the vibrational-state density (Fig. 2). The much more pronounced changes, which have been observed elsewhere⁵ in the Raman scattering spectrum, are caused by the loss of spatial coherence of the vibrations, rather than by a change in their spectrum in the frozen structure. As expected, the most important changes in $G_H(\nu)$ at the transition to the crystalline state occur in the low-frequency part of the vibrational spectrum ($\nu < 300$ cm^{-1}), which is related to external degrees of freedom (to the translational and rotational motion of a molecule as a

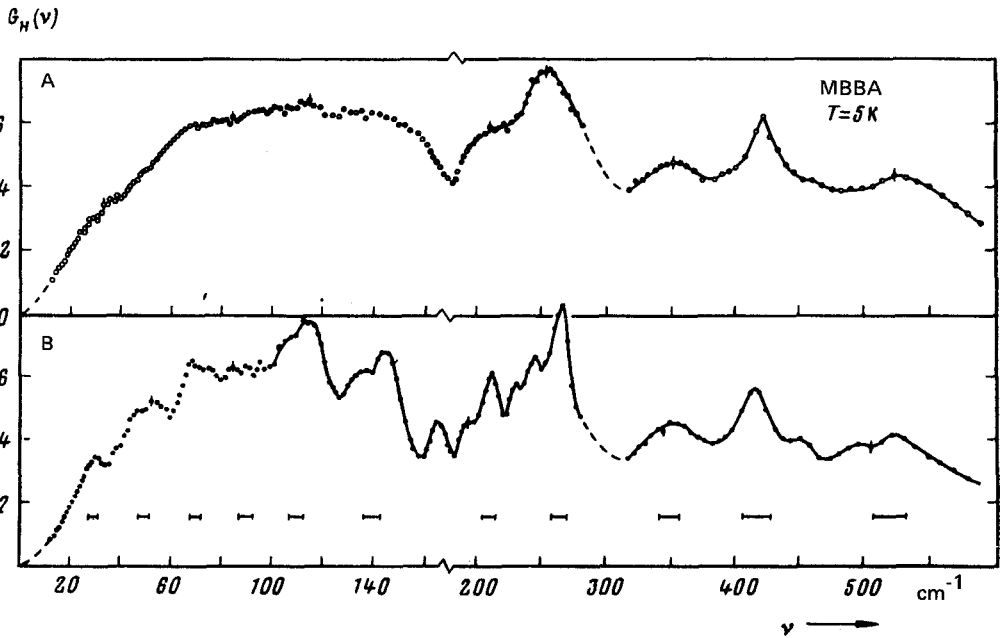


FIG. 2. Weighted vibrational-state density. A—Glassy phase; B—crystal.

whole) and to “soft” intramolecular modes, which are most susceptible to the intermolecular interaction and its changes. The appearance of structure in the function $G_H(\nu)$ for the solid crystalline sample in this region should be attributed to the appearance of distinct phonon bands. These results raise the hope that by measuring the incoherent inelastic neutron scattering spectra of smectic structures at low temperatures, it will be possible to determine the step of the ordering that forms the phonon bands and the required coherence length.

In the region of high-frequency vibrations, $\nu < 300 \text{ cm}^{-1}$, which are associated with internal degrees of freedom, the spectra of the two solid phases are essentially identical (Figs. 1 and 2). The primary conclusion to be drawn from this agreement is that the dispersion of the internal phonons of the MBBA crystal, which retain a molecular nature, is slight. There are nevertheless some detectable differences in the spectra, and these differences raise the question of the shape stability of the molecule upon the formation of glassy and solid crystalline phases.

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¹Neutron structural analysis of MBBA has shown⁶ that a translationally disordered solid of a glassy type is formed in this procedure.

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